[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

Fused "Onium" Salts as Acids. Reactions in Fused Pyridinium Hydrochloride

BY L. F. AUDRIETH, A. LONG AND R. E. EDWARDS

The acidic nature of many of the "onium" ions both in solution and in the fused state, to which attention has previously been called,[1] and the easy solubility of the oxides of the rare earths in fused pyridinium hydrochloride[2] have led us to make a more extended study of the behavior of this latter substance toward metals, metallic oxides and salts.

Pure pyridinium hydrochloride was prepared either by passing dry hydrogen chloride into an ethereal solution of pyridine[3] or by neutralizing an aqueous solution of pyridine with concentrated hydrochloric acid and then fractionally distilling the resultant thick sirupy liquid at atmospheric pressure, collecting the fraction boiling at 219–221°.

The material prepared by either method is a white crystalline solid, insoluble in ether, carbon tetrachloride and benzene. It melts at 144.5° as contrasted with the melting point found by Trowbridge and Diehl[4] of 82°. Analysis shows it to contain 30.53% of chlorine as compared with the theoretical requirement of 30.7%.

Heated somewhat above its melting point, pyridinium hydrochloride exhibited the following behavior.

Metals.—Al, Cd, Ca, Mg, Zn and even Cu react rapidly to form the corresponding chlorides along with hydrogen gas. Mn, Ni, Sn, Pb and Fe also react in the same fashion but less rapidly. As, Hg, Ag and Pt are apparently unaffected.

Oxides.—Sb_2O_3, BaO, Bi_2O_3, CdO, CoO, Cu_2O, CuO, Fe_2O_3, HgO, PbO, MgO, MnO_2 and NiO dissolve readily, forming the corresponding chlorides and water. The pyridine and water can be removed completely by heating moderately under reduced pressure; by heating at still higher temperatures the melts can be concentrated with respect to the metallic chloride by the removal of some of the excess pyridinium hydrochloride.

The acidic oxides MoO_3 and V_2O_5 are very soluble, while WO_3 and U_3O_8 react slowly. Ta_2O_5, SnO_2, ThO_2 and TiO_2 were found not to react.

Salts.—The chlorides of Al, Sb, Cd, Co, Cu^{++}, Fe^{++}, Fe^{+++}, Hg^{++}, Mg, Mn, Ni, Zn are quite soluble in the fused salt. Na, K, Ca and Ba chlorides are only somewhat soluble. In some instances the fusion of metallic chlorides with pyridinium hydrochloride in the proper proportions leads to the formation of the corresponding double chlorides. The melts are simply dissolved in alcohol and recrystallized. $(CoCl_2)_2 \cdot (C_5H_5N \cdot HCl)_5$ and $CuCl_2 \cdot (C_5H_5N \cdot HCl)_2$ were prepared in this way.

Many other salts were found to be markedly soluble in the fused acid, in particular the nitrates (of Be, Ca, Cr and Th). Some carbonates also reacted readily ($BeCO_3$, $CaCO_3$, $PbCO_3$, $MnCO_3$).

Preliminary trials showed that many of the above melts conducted the electric current with facility. Metallic deposits were obtained in the following cases: (1) melts prepared by dissolving PbO, and Sb_2O_3 in fused $C_5H_5N \cdot HCl$; (2) melts prepared by dissolving $AsCl_3$, $BiCl_3$, $HgCl_2$, $PbCl_2$ and $SnCl_2$ in fused $C_5H_5N \cdot HCl$; (3) from the fused double salts, $AsCl_3 \cdot (C_5H_5N \cdot HCl)_3$, $BiCl_3 \cdot (C_5H_5N \cdot HCl)_2$ and $SbCl_3 \cdot (C_5H_5N \cdot HCl)_2$. Attempts to discharge the more active metals were not successful.

These results confirm the above-mentioned generalization with regard to the acidity of the "onium" ion. We have yet to find a single exception to the correctness of this generalization. This behavior is to be ascribed to the action of the "onium" ion as a cation acid rather than to a dissociation of the so-called salt into the anhydro-base and anhydro-acid. This statement is made advisedly in an effort to explain the action of such "onium" salts as ammonium chloride in the vapor state upon metals and oxides. There seems to be no question but that ammonium chloride is completely dissociated in the vapor state. Yet, ammonium chloride reacts quite readily under such conditions with various metals to yield the corresponding chlorides and hydrogen, whereas

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(1) Audrieth and Schmidt, *Proc. Nat. Acad. Sci.*, **20**, 221 (1934); Reed, Hopkins and Audrieth, THIS JOURNAL, **57**, 1159 (1935).

(2) Hopkins and Audrieth, *Trans. Am. Electrochem. Soc.*, **66**, 135 (1934).

(3) An excess of hydrogen chloride must be avoided to prevent the formation of the dihydrochloride which melts at 46.7°. See Kaufler and Kunz, *Ber.*, **42**, 385 (1909); Ephraim, *ibid.*, **47**, 1841 (1914).

(4) Trowbridge and Diehl, THIS JOURNAL, **19**, 568 (1897).

pure and dry hydrogen chloride under identical conditions is without effect upon them.[5] It seems significant in this connection that wet hydrogen chloride is likewise an active agent in corroding these same metals. It therefore seems more plausible to consider momentary recombination of ammonia, or water, with hydrogen chloride on the metallic surface, where both may possibly be absorbed with more readiness, with transient formation of the "onium" ion, which must be regarded as the active agent in causing reaction to take place.

That the reaction between "onium" salts and oxides at higher temperatures is considerably more complicated is self-evident. Here water is one of the products and its formation undoubtedly exerts a marked accelerating effect upon the course of the reaction.

Summary

1. Using a specially purified pyridinium hydrochloride it has been shown that this, as a typical "onium" salt, possesses acidic character in the fused state, reacting with metals and metallic oxides much as does hydrochloric acid in aqueous solution.

2. It has also been shown that many metallic chlorides are soluble in fused pyridinium hydrochloride and form stable low temperature melts. Such melts conduct the electric current with facility and in the case of tin, lead, arsenic, antimony, bismuth and mercury permit the electrodeposition of these metals.

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[5] K. A. Hofmann, Hartmann and Nagel, *Ber.*, **58**, 808 (1925).

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Studies of the Reducing Action of Mercury. I. The Formation of Hydrogen Peroxide in the Interaction of Mercury with Hydrochloric Acid in the Presence of Oxygen

BY N. HOWELL FURMAN AND W. M. MURRAY, JR.

Introduction

In the course of an investigation concerned with further applications of mercury as a reducing agent for certain ions in solutions containing hydrochloric acid, it was observed that a dilute hydrochloric acid solution, when shaken with mercury in the presence of air, acquires reducing properties as indicated by its reaction with ceric sulfate. A large amount of calomel is formed during the shaking of the mixture.

The reaction at room temperature of mercury, oxygen and water to yield oxides of mercury was noted by Fourcroy[1] and has been mentioned frequently in the older textbooks. It has also long been known that a dilute solution of hydrochloric acid attacks mercury in the presence of air, calomel being formed.

$$2HCl + 2Hg + O = Hg_2Cl_2 + H_2O \qquad (1)$$

Such an equation was postulated by Berthelot[2] and has been assumed by other workers. These reactions of mercury and hydrochloric acid in the presence of oxygen were observed and discussed by McCay and Anderson[3] in their work on the reduction of ferric chloride by mercury and also in a later paper by McCay[4] on the reduction of quinquivalent antimony.

Schönbein[5] and Voit[6] reported the formation of "ozon" when mercury is shaken with water and dilute acids in the presence of air. It is now known that the "ozon" to which these workers so frequently refer was in most cases hydrogen peroxide.

Dunstan, Jowett and Goulding[7] found that traces of hydrogen peroxide were formed when mercury was placed under a very dilute solution of sulfuric acid and oxygen bubbled through the liquid for several hours.

The dry reaction between mercury, hydrogen chloride, and oxygen has also been studied, the formation of calomel and oxychlorides of mercury being reported by Berthelot[8] and by Bailey and Fowler.[9]

It has been found in our work that hydrogen peroxide and calomel are formed when samples

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[1] Fourcroy, "A General System of Chemical Knowledge," trans. by Wm. Nicholson, Vol. V, 1804, pp. 431–433.

[2] Berthelot, *Ann. chim.*, [5] **23**, 110 (1881).

[3] McCay and Anderson, THIS JOURNAL, **43**, 2372 (1921).

[4] McCay, *Ind. Eng. Chem., Anal. Ed.*, **5**, 1 (1933).

[5] Schönbein, *Ann. physik. Chem.*, **100**, 1 (1857).

[6] Voit, *Ann.*, **104**, 341 (1857).

[7] Dunstan, Jowett and Goulding, *J. Chem. Soc.*, **87**, 1548 (1905).

[8] Berthelot, *Compt. rend.*, **125**, 746 (1897).

[9] Bailey and Fowler, *J. Chem. Soc.*, **53**, 755 (1888).